CORRELATIONS IN INTERFACES WITH SURFACTANTS.

by

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Abstract

The existence or non-existence of the bending coefficient in liquid interfaces as well as applicability of the Helfrich free energy, is examined by comparing correlations in the interfaces with or without a weak surfactant. In the latter case, the formation of a bilayer is studied and density-density correlations and height-height correlations are reported, analyzed, and compared with "normal" liquid interfaces. In particular the role of lateral tension is discussed.

I. Introduction.

In our previous work we have investigated the structure of interfaces between two immiscible liquids and between a liquid and its vapor[1,2,3]. We used the computer simulation and the method of Molecular Dynamics; the liquids were formed by spherical particles interacting with Lennard-Jones potentials, and only single planar interfaces were studied. It is worthwhile to realize that this was but one particular case and that liquids, in particular multicomponent mixtures, can form a great variety of most exotic phases. One such large group of systems are those containing a surfactant as one component. A very brief review[4] summarizes the basic theoretical understanding of these systems. The references by Nelson et al.[5] and the work of Dietrich and Napiorkowski[6] can additionally be consulted.

In particular, two immiscible liquids on addition of surfactant, can form microemulsions and lamellar phases. These phases, formed often in a narrow range of state parameters (such as temperature T, pressure p, and concentrations $x_1, x_2, ...$) have *many* interfaces in their bulk, held in place by their mutual repulsion among other factors, and are successfully described by assuming their surface tensions to be *vanishing* or almost vanishing. Their fluctuations are therefore ruled not by the ordinary capillary waves and the underlying surface (interfacial) tension, but by the rigidity (bending) coefficient and changes in curvature.

Similarly liquid membranes and bilayers are described by a particular set of concepts such as: area per head-group, spontaneous curvature, bending(rigidity) coefficient and Gaussian curvature. To describe these objects, of great common interest to physicists and biologists, a number of phenomenological theories has been proposed, many of them based on the Hamiltonian associated with the names of Carnam and Helfrich[7].

An immediate question arises: if these membranes, bilayers, and interfaces in lamellar phases, ..., are ruled by their curvatures and associated elasticity coefficients, what about the normal interfaces? Surely they are capable of bending

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and of having non-zero curvature; one therefore legitimately asks for the presence or absence of the same effects in ordinary interfaces. And a related question is : what *is* a "normal" interface and what is a membrane - what is it that makes an interface "normal" and what makes it to be a membrane.

In order to understand better the transition from normal interfaces with non-zero surface tension to those with a vanishing surface tension we have studied immiscible liquids with a third component which is a weak surfactant. Here we report results of MD simulations for an easier and simpler system, a binary system solvent+surfactant in which the surfactant molecules form a single bilayer. Our results include the correlations as given by the structure factor.

In Section 2 we give a simple theoretical introduction, in Section 3 we describe the model and the simulations; then we show and discuss the interfacial structure factors. In Section 4 we discuss the conclusions.

II. Background: free energy, surface tension, and correlations.

The product γA of the surface (interfacial) tension γ and the area A is the contribution of the interface to the total free energy F of the system; thus $F = F_b + \gamma A$ and since γ is positive, lowering of the free energy can normally be achieved by making A as small as possible. Hence the plot of F vs A looks like the straight line labelled (A) in Fig.1. A membrane or a bilayer has an optimal surface area per surfactant head; if $A > Na_h$ the object is stretched, if $A < Na_h$ it is laterally compressed and therefore the *hypothetical* dependence of F on A looks like the curve marked (B) in Fig.1. Once we have admitted such possibilities, various other shapes of $F(A)$ can be invented[5,8]. Still another $F(A)$ dependence is suggested in Section III. Admitting the existence of a minimum in $F(A)$ we reach the unsettling conclusion that the surface tension defined as dF/dA can be positive or negative:

$$A > A_0 \equiv Na_h \qquad \gamma = dF/dA > 0 \qquad (1a)$$

$$A = A_0 \equiv Na_h \qquad \gamma = dF/dA = 0 \qquad (1b)$$

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$$A < A_0 \equiv N a_h \qquad \gamma = dF/dA < 0 \tag{1c}$$

This, however can be understood as follows. Consider a definite setup, like the one illustrated in Fig.2, where the bilayer fills the periodic simulation box, dividing the solvent into the upper and lower parts in the Figure. The interfacial tension can be readily calculated by the Kirkwood-Buff formula[9,10]

$$\gamma = \bar{p}_{zz} - \bar{p}_{xx} \tag{2}$$

where

$$\bar{p}_{\alpha\alpha} = \int_0^{L_z} dz p_{\alpha\alpha}(z) \quad (\alpha = x, y, z) \tag{3}$$

If $\bar{p}_{zz} > \bar{p}_{xx}$ then $\gamma > 0$ and conversely. Of course $p_{yy}(z) = p_{xx}(z)$ by symmetry. There is no injuction against $\bar{p}_{zz}$ being smaller than $\bar{p}_{xx}$. In fact, for a bilayer immersed in a solvent, γ looses its physical meaning developped for normal surfaces. It is directly related to lateral compressibility $K[11]$ by

$$K A_0 = (d\gamma(A)/dA)|_{A=A_0} \tag{4}$$

Such is the quintessential difference between membranes/bilayers and liquid-vapor or liquid-liquid interfaces. For discussions concerning the role of diffusion (particle exchange), various ensembles, different types of bilayers, membranes, and/or vesicles, the specialized literature [4,5,8] can be consulted. Note that when developping a description of Langmuir monolayers, we also change the physical meaning (and the name) of the derivative dF/dA.

Either object can and does fluctuate thanks to thermal motion, and the long wavelength modes are clearly associated with a fluctuation in the surface area A. For normal interfaces the free energy cost of a fluctuation is $\gamma \cdot dA$ and γ in the standard theory does not vary. This leads to the interfacial hamiltonian

$$\mathcal{H}[h] = \frac{1}{2} \int dx dy [\gamma (\nabla h)^2 + V''(0) h^2]. \tag{5}$$

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and to the height-height correlation function (in Fourier-transformed form)

$$<\mid h_q \mid^2> = \frac{kT}{\gamma q^2 + \gamma \xi^{-2}} \tag{6}$$

where the parallel correlation length is

$$\xi^2 = \frac{\gamma}{V''(0)} \tag{7}$$

If the capillary-wave, or interfacial, hamiltonian is improved by further terms, so the denominator in (6) contains more than just γq^2. Offhand one expects this term to be the second term D_2 in the power series such as $D_0 + D_2 q^2 + D_4 q^4 + ...$ but Dietrich and Napiorkowski[6] have shown that such a power series diverges and should be replaced by $D_0 + D_2 q^2 + D_4 (q^4 \log q) + ...$ It is therefore safer to write

$$1/ <\mid h_q \mid^2> = D_0 + \beta \gamma q^2 + q^4 f(q) \tag{8}$$

with $\beta = 1/kT$, $D_0 = \beta V''(0)$, $D_2 = \beta \gamma$, $f(q)$ unknown. Mecke and Dietrich[12] defined the combination $\beta \gamma + q^2 f(q)$ as the effective surface tension $\beta \gamma_{eff}(q)$ and based their calculation on the density functional theory in which the rotation of the fluctuating density profile was (for the first time) accounted for. Calculations become straightforward if using the approach pioneered by Robledo et al. [13], based on the interfacial hamiltonian derived in a clear way from the exact second-order free-energy difference due to density fluctuations $\delta \rho(\mathbf{r})$ in terms of the Inhomogeneous Direct Correlation Function $C(1, 2)$

$$\delta F = (1/2) \int \int d(1) d(2) C(1, 2) \delta \rho(1) \delta \rho(2) \tag{9}$$

from which, in one approximation

$$\mathcal{H}[h] = \sum_{\mathbf{q}} \bar{C}(\mid q \mid) h_{\mathbf{q}} h_{-\mathbf{q}} \tag{10}$$

and

$$1/ <\mid h_q \mid^2> = \bar{C}(q) \tag{11}$$

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The function $\bar{C}$ of one variable q is a projection of $C(z_1, z_2, q)$ [13]. We have determined[3] this function from our simulations[3] and we have shown unequivocally that (a) there exists the initial region $q \in [0, q^*]$ where $C(q) = C_0 + q^2 C_2$ - i.e. the region of capillary waves (b) that is terminated by a sharp maximum near $q^* \sim 1\sigma$ after which $C(q)$ falls to reach a broad minimum near $q \sim 2\pi/\sigma$. If one wishes to construct a power series $C = C_0 + C_2 q^2 + C_4 q^4 + ...$ it is clear that C_4 *must be negative* and moreover from the general discussion of Stecki[3] it follows that it is *a general feature* of the liquid-vapor interface. We can also make contact now with the theory of Mecke and Dietrich[13] and with the experimental results [14] where the concept of the effective interfacial tension in the sense of eq.(8), is used. From our data of $\bar{C}(q)$ we can construct this quantity by the simple division by q^2: $\beta\gamma_{eff}(q) = (\bar{C}(q) - \bar{C}(0))/q^2)$. Another possible definition could jus as well be $\beta\gamma_{eff}(q) = (d/d(q^2))\bar{C}(q)$. Figure 3 shows the plot of $\beta\gamma_{eff}(q)$ and the characteristic fall with the increase of q; the confirmation of this result by recent experimental data [14] is very gratifying. These result also mean that all attempts to interpret C_4 as a kind of bending coefficient are doomed because C_4 is going to be *always* negative in a liquid-vapor interface. In a liquid-liquid interface[1] the agreement with the standard capilllary-wave theory was excellent but the extraction of the D_4 term was not so unequivocal (though a renewed interpretation of our data with the aid of the theory of Dietrich and Napiorkowski[6] remains to be done).

Such was one way of representing and interpreting the scattering factor $S(q) \sim <| h_q |^2>$, *i.e.* through a representation

$$1/S = D_0 + D_2 q^2 + D4 q^4 + ... = D_0 + D_2 q^2 + q^4 f(q). \tag{12}$$

Quite another representation has been used[11] for the height-height correlation function of a simulated bilayer, namely

$$S(q) \sim a/q^4 + b/q^2 \tag{13}$$

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We do not know of any theoretical justification of this form. For normal interfaces statistical mechanics predicts eq.(6) as "the most divergent term"[9,10]. It is a broader issue we do not address in this paper. Certainly, as an empirical formula (13) is very successful and in what follows we have applied both of these representations to our new data on liquid bilayer formed by a weak surfactant in a one-component solvent. We generalize (13) in an obvious manner

$$S(q) \sim a/q^4 + b/q^2 + A + Bq^2 + ... \tag{14}$$

Section III. The modelling of interactions and the results.

We use the model of spherical particles interacting with the Lennard-Jones (6,12) potentials with cutoffs. In order to have the simplest posssible system without obscure complications we choose equal masses and equal sizes but different cutoffs in the spirit of WCA theory, used often in other work[15,16] The interaction potential is

$$u_{\alpha\beta}(r_{ij}) = 4\epsilon[((\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6)) - ((\sigma/r_{\alpha\beta}^c)^{12} - (\sigma/r_{\alpha\beta}^c)^6))] \times \eta(r_{\alpha\beta}^c - r_{ij}) \tag{15}$$

with species index $\alpha = 1, 2$ for species "a" and "b", respectively and similarly for species index β. $\eta(x)$ is the Heaviside function. The cutoff distance is $r_{\alpha\beta}^c = 2.5\sigma$ if $\alpha = \beta$ and $r_{\alpha\beta}^c = r^* \equiv 2^{1/6}\sigma$ if $\alpha \neq \beta$. We model the surfactant as a dimer made of unlike particles which interact with monomers according to the same interaction potential. The inner bond interaction is $u_{12}(r)$ if $r < r^*$ and $u_{12}(2r^* - r)$ if $r > r^*$. I owe the suggestion of this model to S.Toxvaerd[17]. But it was Smit[18] who first modelled in a simulation the surfactant as a dimer and has shown it already has some semblance to reality.

The "standard" version of our model is the one with equal masses and with the same ϵ for all pairs. The solvent is made of "a"'s, and the bilayer is made of bound "a-b" pairs. Therefore the "a" end of the dimer plays the role of the "head" in contact with the solvent (since the a-a pairs are favored energetically) and the

"b" end of the dimer plays the role of the hydrocarbon part and likes to stay inside the bilayer, away from the solvent. This is already seen in Fig.2. We have also investigated a few modifications. First, the heads are often polar as is the solvent whereas the cohesive energy of hydrocarbon environment is low; thus we can make the "a"free - "a"bound interaction stronger than the rest. This did not enhance the formation of the bilayer in any visible way but it did result in filling the bilayer with solvent, to a large extent. We can also make the "b"-ends heavier to slow down the motions of the bilayer. Finally, we can add an additional repulsion of longer range between the "b"ends and the free "a"'s so as to presumably chase any solvent particles out of the inside of the bilayer; the latter interaction can be a repulsive r^{-9} potential[11]. In the end, we did not continue with these modified versions because the essential features of the bilayer were not changed much. We did some simulations with a long-range repulsive potential [11], because we found it enhanced the q^{-4} contribution to the scattering factor $S(q)$ (cf. eq. (13-14)).

We report here simulations with a periodic box with N=40,000 particles and $N_d = 1440$ dimers, with box dimensions about $30 \times 30 \times 50$, at temperature $kT/\epsilon = 0.75$. The Molecular Dynamics was performed with Verlet leap-frog algorithm and Nose-Hoover thermostat[19]. The preassembled bilayer adapted its own configuration very quickly but, as we started from a surface area 50×50 the surfactant dimers aggregated into domains.These grew in time, though very slowly. An x, y projection of an early structure with domains are shown in Figure 4. If left to equilibrate, a large connected domain resulted and one or two big holes filled with solvent. This suggested that there might exist the membrane-like quantity, the area per "a"-head. Compressing the system in the lateral x, y directions with a simultaneous expansion in the z-direction changes the surfactant domains and eventually the x, y cross-sections become homogeneous at an area at which γ is still positive. This is reminiscent of the two-dimensional domain coexistence, known very well for monolayers. If so, the $F(A)$ dependence might have a shape like the double inflexion curve "(C)" in Fig.1. Further lateral compression brings

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about an increase in $\bar{p}_{xx} = \bar{p}_{yy}$, and a decrease in $\bar{p}_{zz}$, hence a decrease in γ and a change in the x, y morphology. . Further compression diminishes γ and eventually very low values of γ can be reached. Such states appear to be stable. Compression to still lower areas produced negative γ but such states were not stable. It was found possible to maintain a bilayer with γ about -0.01. The bilayer reorganized itself doubling its thickness in most cases and restoring γ to positive values. Also it was not clear whether the bilayer with slightly negative γ was not a metastable state. It would persist for 1.E6 timesteps but this is no proof. The reorganized bi-to-quad layer was very stable. We have taken the view that the positions of the centers of mass of the dimers determine the instantaneous surface[5], or rather two instantaneous surfaces of "up-dimers" and "down-dimers". From these two correlation functions were constructed, the dimer-dimer density-density correlation function

$$H_{dd} = < \rho_d(\mathbf{r}_1)\rho_d(\mathbf{r}_2) >$$

or rather its two-dimensional Fourier transform $H(q)$ and the height-height correlation function $S(q) \equiv < h_q h_{-q} >$. Each z-coordinate of a dimer is treated as height $[x, y, z] \rightarrow [x, y, h(x, y)]$. For each set of positions at given time, the average heights are calculated and the actual heights are measured with respect to this instantaneous average. These two functions do not differ much so we choose S(q), for the discussion. We wish to discriminate between the two mathematical forms, (12) and (14). We note that (13) can be rewritten as $(a + bq^2)/q^4$ which implies a limit of the expression $S(q)q^4$ and therefore we have analyzed the following quantities: S, Sq, Sq^2, Sq^3, Sq^4, and their inverses. Taking the limit $q \rightarrow 0$, for damped $(D_0 \neq 0)$ and free $(D_0 = 0)$ case we calculate the limits of the analytical forms (12) and (14) and test these detailed predictions on our data. The expressions (12) and (14) lead to different behaviour of such derived functions, as $q \rightarrow 0$. First, Fig.5 shows a plot of the height-height correlation $S(q)$ for a bilayer with a small positive γ; due to smallness of the capillary-wave contribution, the plot is dominated by the approach to the first nearest-neighbor peak seen near $q = 2\pi/\sigma$.

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The capillary-wave divergence is very weak. Out of the analysis outlined above we show only one plot in Fig.6; if the "traditional" expression (12) were appropriate, plot of Sq^2 vs. q^2 ought to be linear with value at zero $D_2 = \beta\gamma$ and slope $D_4 > 0$. Clearly this is not the case. Alternatively, expression (13) requires that Sq^4 should reach a constant and for data shown in Fig.5 and Fig.6 this is not the case. After the analysis we found that data in Fig.5 and 6 are well represented (for not-too-large q) by (14), though *with a=0* i.e. by $S \sim b/q^2 + A + Bq^2$.

V. Discussion

Our results seem to confirm the view expressed above, namely that the membrane-like approach to interfaces is valid if there exists a series of stable states with a minimum of free energy at a surface area A_0 of a tension-free bilayer. For our weak surfactant modelled by a dimer, it appears that the compressed states with $A < A_0$ are not stable, and the expanded states, are stable within a narrow range of areas. For higher A's the bilayer breaks into domains. For lower A's it reorganizes itself into a quad-layer with a positive γ. Then the expected bending modes *either* in (12) ($D_4 \neq 0$) or in (13)-(14) ($a \neq 0$) do not show. It may well be, in line with the qualitative discussions[20] that a long chain-length or a double chain-length is needed for a formation of a stable bilayer, i.e. such that would be stable in an interval of areas including the equilibrium tensionless state, compressed states, and expanded states. Such a bilayer was constructed[11] but it is now not clear what was the role of the additional special repulsive (r^{-9}) potential introduced in that work[11], in stabilizing the expanded and compressed states. Finally, we find it relatively straightforward to determine the density correlation functions such as those reported here.

References

[1] J. Stecki and S. Toxvaerd J. Chem. Phys. **103:**9763 (1995).

[2] J. Stecki J. Chem. Phys. **107:**7967 (1997);*ibid.* **108:**3788 (1998).

[3] J. Stecki J. Chem. Phys. **109:**5002 (1998).

[4] G. Gompper and M. Schick, vol. 14 of *Phase Transitions and Critical Phenomena:*C. Domb and J. Lebowitz, Editors, Academic Press, London (1995).

[5] D. Nelson, T. Piran, and S. Weinberg, Editors, *Statistical Mechanics of membranes and Surfaces:*World Scientific, Singapore, 1989.

[6] S. Dietrich and M. Napiorkowski Z. Physik B **89:**263 (1992); Phys. Rev. E **47:**1836 (1993).

[7] W. Helfrich, Z. Naturforschung **28C:**693 (1973).

[8] L. Peliti, in *Les Houches, Session LXII, 1994, Fluctuating Geometries...* (Elsevier, New York, 1995); where further references to original papers can be found.

[9] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford,1982).

[10] R. Evans, in *Les Houches, Session XLVIII, 1988, Liquids at Interfaces* (Elsevier, New York, 1989); see also Adv. Phys. **28:**143 (1979).

[11] R. Goetz, G. Gompper, and R. Lipowsky Phys. Rev. Lett. **82:**221 (1999).

[12] K. R. Mecke and S. Dietrich Phys. Rev. E **59:**6766 (1999).

[13] V. Romero-Rochin, C. Varea, and A. Robledo, Physical Review A **44:**8417 (1991); Physica A **177:**474 (1991); *ibid.* **184:**367 (1992).

[14] J. Daillant et al. preprint 1999 and European Physical Society Conference on Liquids, Granada 1999.

[15] Toxvaerd and Velasco Mol. Phys. **86:**845 (1995).

[16] M. Laradji, S. Toxvaerd, and O. G. Mouritsen Phys. Rev. Lett. **77:**2253 (1996).

[17] S. Toxvaerd, private communication.

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[18] B. Smit Phys. Rev. A **37:**3431 (1988) and B. Smit, A. G. Schlijper, L. A. M. Rupert, N. M. van Os J. Phys. Chem. **94:**6933 (1990) for a model of surfactant.

[19] S. Toxvaerd Mol. Phys. **72:**159 (1991).

[20] J. Israelashvili, "Surface and Intermolecular Forces", Academic Press, 1994.

Figure Captions

Figure 1.

Total free energy dependence on A, the area of the interface or of the membrane-like object. (A) is the normal interface: $F = F_b + \gamma A$ and γ, the slope, is const. (B) is what is predicted for a membrane-like object for which $F(A)$ hs a minimum at a specific area-per-head. (C) is the general shape if coexistence of domains is assumed. Then γ is constant in the two-phase region.

Figure 2.

A typical snapshot configuration of a bilayer; the "a" ends of dimers are marked with diamonds, the "b" ends are marked with crosses, and the free "a"'s (the solvent particles) are not marked for clarity. Here $kT/\epsilon = 0.75$ and there are 1440 dimers; the lengths are in units of Lennard-Jones σ - the collision diameter of the molecules.

Figure 3.

The "effective q-dependent surface tension" calculated by dividing by q^2 the function $\bar{C}(q)$ discussed and shown earlier[3]. Its shape as function of q is identical with that found in a real experiment [14] and calculated from the density-functional theory with rotation of intrinsic profile, except for the limiting region $q \to \infty$ where in our case the finiteness is ensured by the general properties of the Ornstein-Zernicke function c for $r_{12}- > 0$.

Figure 4.

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Lateral domains of surfactant heads and tails formed when the surface area is too large and the bilayer would be under stretching tension, were it homogeneous. Solvent molecules, which fill the holes, are not shown for clarity. All data shown are for N=40000, $T^* = 0.75$, and the "standard" model described in Section 3.

Figure 5.

A typical plot of $S(q)$ vs. q for a bilayer (nearly tension-free i.e. with γ near zero). Note the position of the first peak near $q = 2\pi/\sigma$, and the barely visible capillary-wave (or bending wave) divergence near $q = 0$.
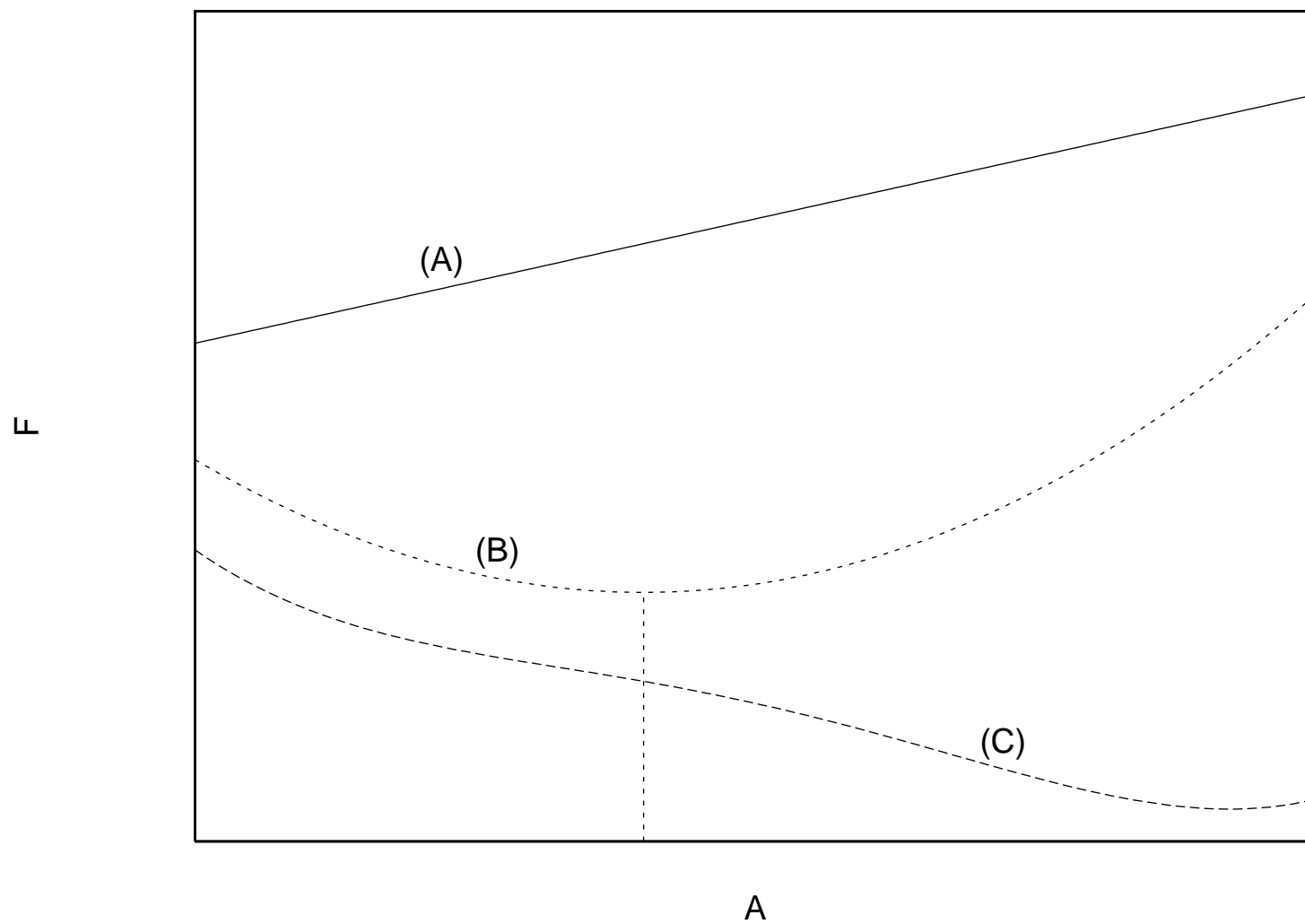
Figure 6.

A typical plot of $1/S(q)/q^2$ vs. q^2.

F

(A)

(B)

(C)

A

Fig2